

16th DOE NUCLEAR AIR CLEANING CONFERENCE

Session 6

CRITICAL REVIEW

TUESDAY:      October 21, 1980

THE EVOLUTION AND CURRENT STATE OF RADIO-IODINE CONTROL  
J. Louis Kovach

THE EVOLUTION AND CURRENT STATE OF  
RADIO-IODINE CONTROL

J. Louis Kovach  
Nuclear Consulting Services, Inc.  
Columbus, Ohio

Abstract

The history, development, and problems existing in the US nuclear power reactor iodine clean-up technology are discussed. The areas of iodine transport in containment, adsorbent types, impregnation effects, mechanical and testing problems are reviewed, particularly in view of the TMI-II accident. The problems resulting from the fragmentation of responsibility and the very slow transfer of technology from research to application are pointed out.

I. Introduction

Among fission products probably Iodine 131 and its compounds have been most extensively evaluated. Its generation, release mechanism, properties, forms, trapping and retention behavior and health effects have been the subject of numerous studies in the past and present. At the same time, a comprehensive understanding of its realistic release significance and an integration of the chemical technology into the protection technology is lacking. By far the larger portion of the work reported in the literature treated a narrow segment of the iodine technology, and often under conditions which are not realistic in power reactor applications. This review will attempt to tie together theoretical studies with practical experience, while pointing out the gaps in current understanding requiring further evaluation.

II. Iodine Generation and Release

While the generation of iodine isotopes during the burn-up of nuclear fuel is a reasonably well understood and calculatable phenomenon, its release and transport from failed fuel is not.(1) (2) Early reactor protection systems consisted of particulate filters of various efficiency. Iodine release during the Windscale accident in 1957 resulted in an effort to control iodine dispersion into the atmosphere. However, major differences exist between the evolved US power reactor types and the Windscale reactor and, unfortunately, between many of the laboratory experiments performed in the US to study fission product release and actual reactor operating experience.

The postulation that the water reactor accident will result in the release of iodine according to the NRC source term is unlikely. While the Windscale core being a gas-cooled reactor indeed released about 20-30,000 Curie of iodine mainly in elemental and perhaps some organic form, releases from the water-cooled reactors will be primarily in iodide form from the core and only a small fraction will convert to volatile form under ambient conditions, most of which will be organic.

Failure of the water cooled reactor fuel under accident conditions will result primarily in the release of CsI which has a boiling point of 1280°C and a

melting point of 621°C. It is very soluble in cold, hot and alkalized water and would be converted to elemental iodine only upon exposure to acidic or oxidizing atmospheres which, in view of water reactor coolant chemistry, are unlikely events.

Some partitioning into organic forms will be inevitable based on the presence of various hydrocarbons both in the gaseous and liquid phase of the post accident containment. The current assumptions of USNRC Regulatory Guides 1.3 and 1.4 are incorrect and, aside from the siting and overall accident evaluation, resulted - not necessarily by themselves, but by their preceding documents WASH-1400 etc. - in incorrect directions for technology development:

- 1) for control of iodine within the containment, and
- 2) for control of iodine release to the outside atmosphere.

The net effect is that:

- 1) much less elemental iodine will be released to the containment atmosphere than expected as indicated by the TMI-II accident (and other water-cooled reactor accidents);
- 2) most of the iodine will be in iodide form and will stay in the water phase;
- 3) most of the iodine in the vapor phase will be in organic form.

While the above criteria is based on serious accident mode, the release path would be similar for operational releases also. Thus the actual health effect of iodine 131 is significantly less than expected and the control technology is somewhat misapplied because it is based on the assumptions which resulted from experiments performed under unreal conditions.

### III. History of Iodine Control

The first major US effort relating to iodine control consisted of design studies for the NS Savannah and the Hanford N reactor confinements.(3)(4)(5) At that time, primary interest existed in elemental iodine control mainly because other forms were not identified and the lack of data analysis differentiating iodine forms from various prior accidents. While the US effort was toward ventilation problem-solving, an early and very realistic analysis was presented by Riley (6) at the Seventh Air Cleaning Conference which proposed more of a process engineering solution to iodine control, recommending 1 foot deep carbon beds operated at high velocity resulting in an 0.5 seconds residence time. Unfortunately, in the US the HVAC concept persisted and shallow beds of carbon became the predominant iodine control method.

The design was based on relatively short term laboratory experiments, with fresh carbon, under artificially clean and arbitrary iodine inlet conditions. (7)(8)(9) The results indicated phenomenally high iodine removal efficiency for 2.0 - 2.5 cm carbon beds typically arranged in pleated form and containing 20.0 - 25.0 kg carbon for each 5m<sup>3</sup>/sec air flow (10)(11)(12)

This technology existed into the mid to late sixties until the improvement in measurement techniques and analytical methods identified organic iodides and

it was found that, under high humidity conditions, the shallow carbon beds were incapable of removing organic iodides, particularly methyl iodide.(13)(14)(15) The somewhat accidental discovery that isotope exchange works on carbon surfaces also, and that gas mask carbons impregnated with tertiary amines to control low molecular weight war gas organic halides also reacted with radioactive organic halides, led to the utilization of stable iodine or stable iodide impregnated carbons to control  $\text{CH}_3^{131}\text{I}$  by isotope exchange and amine impregnated carbons to control methyl iodide by complex formation.

However, while laboratory experiments with unimpregnated carbons indicated that 2.5 cm bed depth performed acceptably for short duration while new, the performance of the impregnated carbons for  $\text{CH}_3^{131}\text{I}$  removal indicated a minimum acceptable bed depth, under ideal conditions, to be 5.0 cm, i.e. an 0.25 second residence time. Thus the tray concept was utilized by tying two military type 50 mm deep, approximately 610 x 610 mm face area adsorbers to a single face plate.

Unfortunately, standardization of the external dimensions of the tray type units were developed too late and, even currently, approximately ten different adsorber sizes exist in the US, creating a logistics nightmare for spares or replaceability in case of an accident. As an example, on the TMI site between the two reactors, there are four different adsorber shapes and sizes, three of them supplied by the same adsorber vendor.

The application of the adsorbent media was also somewhat haphazard, because it was found that  $\text{KI}_3$  ( $\text{KI} + \text{I}_2$ ) impregnated carbon performed in a short term test better than unimpregnated carbons, their application predominated the early iodine control technology in the US. These carbons, depending on the method of preparation, resulted in varying pH properties of the finished carbon from neutral to acid pH of the water extract. Naturally the original carbon water extract pH also influenced the final product pH. In this respect, the use of vegetable base (coconutshell) carbons was fortuitous because these carbons, besides possessing high hardness, also contain approximately 1.0%  $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  which, by reacting with free elemental iodine, result in less easily migrating iodide forms.(16)(17)(18)

The late sixties, early seventies resulted in the realization that the carbons used were indiscriminately adsorbing other organic compounds and were subject to "poisoning", thus the design data based on short term fresh carbon experiments were not realistic for the long term protection expected from the carbon beds. This observation spurred on the development of so-called deep bed adsorbers which contain 10 - 50 cm deep impregnated carbon sections and eliminate multiple gasket leaks. (19)(20)(21)(22)

It was also during this time that a theoretical postulation of the post accident iodine release and transport concepts became codified instead of verified. The assumption that large quantities of elemental iodine would have to be cleaned up under somewhat unrealistic conditions resulted in the design concepts used today. These criteria were that 50% of core iodine is released, 50% of that plates out and of the remaining volatile 25%, the breakdown is 85% elemental, 5% particulate and 10% organic form.(23)(24)

The various regulatory criteria resulted also in the segregation of filter-adsorber systems into engineered safeguard and other equipment without thorough understanding of potential accident modes and the availability of systems to treat potential iodine release.(25)(26)

The final concepts developed relate to treating large diluted air volumes several steps away from the generation of the iodine fission products. Rather than using iodine getters in core, removing iodine from coolant or released water (or from the spent fuel storage pool), the iodine is captured after release and dilution into the gaseous atmosphere at a great expense, because of the large volumes of air used and because of the presence of a large quantity of other chemicals in the air which compete by coadsorption or reaction with the impregnants.

### IV. Adsorbent Types

Most of the adsorbents used, particularly the early ones, were developed and evaluated on a trial and error basis. Review of data of early iodine or methyl iodide decontamination tests indicate random properties and a large number of random experiments, where after performance of a hundred tests, one could not predict results of the hundred and first. Even today, the effects of such critical parameters as adsorbent surface area or optimum pore size are unknown.

Among the carbon types, the US development was based primarily on coconut-shell carbons. While the pore structure of reconstituted carbons is preferred because of the presence of intermediate and macro pores, enhancing diffusion, which is the rate controlling step, particularly in the range of air velocities used in carbon beds. These reconstituted carbons typically are coal or petroleum based and contain much larger amounts of sulfur than coconut carbons. This sulfur content, during the time of use, results in the generation of sulfur dioxide which can react with the iodine impregnant and also result in acidic conditions, causing iodine migration through the carbon bed. The sulfur present in these carbons is very difficult to remove and can typically be counteracted only by the addition of excess alkali.

The presence of alkali salts, whether naturally occurring as in coconutshell carbon, or added separately during the impregnation step, helps the fixation of adsorbed iodine by reaction to iodide. However, the same alkali compounds also catalyze carbon oxidation and excess alkali will lower the ignition temperature of the carbons.(27)(28)(29)(30)

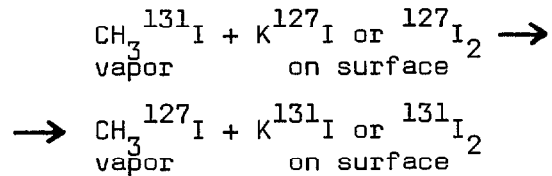
Other noncarbonaceous adsorbents used are typically substrates for silver or lead compounds; these are zeolites, silicas or alumina-silica composites. These adsorbents are typically more sensitive to water adsorption at high humidity, but have the advantage of being nonflammable, which permits their use in oxidizing environments. Without an impregnant they are inferior to carbon, even for elemental iodine removal.(31)(32)(33)

The unimpregnated carbons show a high initial efficiency for removal of elemental iodine from an air or air/steam mixture at low temperatures, particularly when the carbon is not loaded with other organics (7)(9). However, significant migration, i.e. desorption, is observed for several carbons at temperatures in the neighborhood of 180°C, particularly in a radiation field. This phenomenon would be expected to be accelerated when the carbon contains other adsorbed organic compounds, when in fact it can act as an organic iodide generator by the reaction of the adsorbed iodine and various organic compounds.(30)(39)

The initial impregnants used in the US were  $KI + I_2$  ( $KI_3$ ). Depending on the impregnation technique used, these adsorbents had various ratios of  $KI$  and  $I_2$  deposited on the carbon surface in quantities of up to 5% by weight of the base  $I_2$

carbon.(35)(36)

The primary process of organic iodide decontamination on these carbons is by isotope exchange:



as long as sufficient stoichiometric excess stable iodine is present in the adsorbed stage. For the exchange to take place, the following steps are required:

- 1) diffusion to the grain surface (bulk diffusion),
- 2) diffusion into the pore structure (pore diffusion),
- 3) adsorption,
- 4) isotope exchange,
- 5) desorption,
- 6) diffusion out of the pore structure,
- 7) diffusion into the gas phase.

Evaluation of the exchange rates at constant residence time, but varying superficial velocity, indicates that below 10 cm/sec bulk diffusion is the rate controlling step, above 40 cm/sec pore diffusion is the rate controlling step, while the intermediate range between 10 - 40 cm/sec is a transition range between the two rate controlling steps, depending on particle size, micro and macro porosity, temperature, etc., which factors normally influence diffusion rates. (37)(38)(39)

Unfortunately, most US systems are designed for approximately 20 cm/sec superficial velocity, thus fall into the steep slope, intermediate range, where small changes in superficial velocity can strongly affect the DF through the adsorbers.(25)

The iodine impregnated carbons similarly to others have been evaluated mainly in short duration experiments and the potential problems of long term use have not been appreciated. Taking an example of a small PWR, with a core inventory of 9.2 kg of iodine, which would be released mainly as CsI in case of a serious accident, the iodide would plate out or be partitioned into the water phase. However, the reactor has a containment recirculating filter system containing approximately 10,000 kg of KI<sub>3</sub> impregnated carbon with about 100 - 150 kg of free stable iodine which, due to migration in the post accident time, can be released into the containment. By isotope exchange, observed in several experiments, this will result in a significant increase in the airborne <sup>131</sup>I concentration, which is not bound any more to the cesium and cause a potential subsequent increase in the airborne organic iodide fraction.(40)(41)

Aside from these radiological consequences, the free iodine will be very corrosive in the near 100% humidity post accident environment, the stainless steel screens of the adsorber will fail, and iodine-containing carbon grains can

be transferred into the liquid radwaste systems through the drains.(42) In the respect of either of these scenarios, it is difficult to justify the use of impregnated carbons when the carbon is acidified due to aging oxidation, or contamination from the environment inside the containment.

If iodine or iodide compounds are impregnated on the activated carbon, the least that should be done is to incorporate a buffering compound which maintains an alkali pH for a longer period of time.(40)

The use of tertiary amine impregnants has been started in the UK (15)(44) and gained acceptance in the US in the early seventies, mainly in the form of coimpregnation with KI.

The use of 5% TEDA on carbon as practiced in the UK and other European countries has been found inappropriate on coconutshell carbons, because of the low flash point of the TEDA and the relative volatility of TEDA from carbon in continuously flowing air streams. Most US TEDA applications were in 1.0 - 2.0% TEDA, 1.0 - 2.0% KI coimpregnant form with various buffering and fire retarding agents added.(28)(37)(45)

The use of other tertiary amines with side chains permitting stronger retention on the activated carbon came into practice in the US only in the last three years. These compounds, while capable of complexing with methyl iodide as strongly as TEDA, are retained more strongly on activated carbon and maintain both longer life and higher flash point when heated.(46)

In place test indications are that tertiary amine impregnated carbons poison slower than carbons impregnated with iodine alone and permit less migration of the adsorbed iodine even when partial poisoning took place. (43)(47)

The optimum impregnants probably have not been found yet, and development of proper base carbon-impregnant combinations which bring together the best of both properties should be one of the research goals of the future.

Regardless of the particular impregnant used, when complexing with methyl iodide takes place, the process is non-selective as far as isotope type is concerned, thus the tertiary amine will complex with all forms of methyl iodide.

The following steps are required for completion of the process:

- 1) diffusion to the grain surface,
- 2) diffusion into the pore structure,
- 3) adsorption,
- 4) chemical reaction.

Because the steps are fewer for completion of the process, at equal residence time higher methyl iodide removal efficiency can be obtained with amine complexing than with the isotope exchange process.

While the major removal paths are reasonably well identified, other reactions between the methyl iodide and the carbon surface or compounds adsorbed on the carbon surface take place, such as hydrolization of the  $\text{CH}_3\text{I}$  to  $\text{CH}_3\text{OH}$  and possible others not currently identified.(47)(48)

V. PARTICLE SIZE EFFECTS

The US regulatory criteria for particle size distribution established an 8 x 16 mesh product, with limits of 40 - 60% for the 8 x 12 and the 12 x 16 fractions. For precise evaluation, it has to be remembered that even slight shifts in particle size distribution will have an effect. In all cases the presence of smaller particles will increase efficiency because both bulk and pore diffusion are faster for smaller diameter grains.

VI. TEMPERATURE EFFECTS

The earlier assumptions were that impregnated activated carbons perform well at low temperatures even at very high humidities, while the performance falls off in the neighborhood of 130°C, if the humidity rises above 90%.(19)(36)(37)(50)

Data generated subsequent to establishment of precise temperature and humidity control in beds not subject to flooding or wall effect showed that carbons in fact perform better at 130°C even at 95% RH, which corresponds to the post LOCA steam/air mixture and the most critical test to evaluate adsorbent performance for efficiency is at ambient temperature (25° to 30°C) and high humidity (95% RH).

This is expected from the effect of temperature on all of the rate controlling steps, because both types of diffusion and even chemical reaction rates increase with increasing temperature.

However, the adsorption strength (retentivity) decreases with increasing temperature, and particularly in case of the presence of free elemental iodine forms on the carbonaceous adsorbent, iodine will start to desorb as the temperature is elevated.(50)(51)(52) The test criterion for evaluating new adsorbents is a short term exposure of <sup>131</sup>I loaded carbon to 180°C and measurement of the retentivity. It should be realized that, as the carbon is "poisoned", the retentivity for iodine will decrease.(28) As it was stated earlier, one of the most influencing factors on retentivity is the free alkali content of the carbon.

Silver containing adsorbents have good retentivity at higher temperatures than activated carbons. Where exposure above 150°C is expected and, particularly if an oxidizing environment exists, carbon base adsorbents should not be used.(53)(54)

The ignition temperature of new carbons used for nuclear air cleaning is to be above 330°C at high air velocity (50.8 cm/sec) in a shallow (2.5 cm) bed. While this is not difficult to achieve, the following problems can arise under actual conditions:

- 1) The ignition temperature will be lower in deeper beds.
- 2) The ignition temperature will be lower at lower velocities.
- 3) The ignition temperature will be lower when various organic compounds are adsorbed on the carbon bed.

While numerous programs have been written of fire control by airflow cooling (55)(56), the fact that one of the worst solutions is feeding low



velocity air through heated carbon beds has to be considered, because insufficient cooling occurs, while sufficient oxygen is fed to promote further oxidation.(57)

#### VII. Aging and Poisoning

The major paths resulting in poisoning the impregnated adsorbents have been identified. These are:

- 1) organic solvent contamination,
- 2) inorganic acid gas contamination,
- 3) formation of organic oxides in the carbon surface,
- 4) formation of  $\text{SO}_2$  from carbon sulfur content.

The degree of poisoning depends on both internal and external environmental factors in the use location, such as amount and type of organic solvents, paint, etc. used, and the manner of their venting, and location of coal burning power plants or other inorganic pollutant generating facilities in the immediate vicinity of the nuclear power station.(58)(59)(60)

Predicting useful life of the adsorbent can rarely be transposed from the experience of one facility to another. Only the rather generic prediction can be made, that average useful life of the impregnated carbons is based on the quantity of contaminated air passing through the carbon. Typical lives to 90% efficiency under ambient temperature high humidity conditions, for continuously operated 5.0 cm deep beds is six to twelve months. For standby or intermittently operated systems, the life is longer, but prediction of useful life is more difficult because of the transients of contaminant loading.(43)

In all cases, low molecular weight, low boiling point organic compounds have a limited adsorbed state on the carbon and, even if causing temporary poisoning, will desorb from the carbon, while high molecular weight organic compounds will be very strongly adsorbed on the carbon and will cause permanent poisoning.

The acidification of the impregnated carbons can be very easily followed by pH measurement of the water extract. Carbons should be changed out when the pH level falls below 7.0.(16)

Numerous studies were performed to evaluate specific cases of poisoning which could be subject to interpretation to other specific locations without generalization.(61)(62)(63)(64)(65)(66)

Naturally, the poisoning will progress from the side of the carbon bed facing the air flow and such poisoning lowers or destroys the organic iodide removal efficiency of only a narrow band of the carbon bed on the inlet side. This band will widen with time, therefore, adsorbent beds deeper than 5.0 cm, will be progressively efficient longer with increasing bed depth. However, even if the poisoning contaminant is only intermittently generated and the band does not widen in a steady state manner, the poisoning compound will migrate slowly through the adsorbent.

The ideal theoretical system is where the air inlet side of the adsorbent is progressively removed and unpoisoned adsorbent is available for iodine control.

Such systems are difficult to design and several compromise solutions are practiced, such as very deep unsegregated beds, separate guard beds containing different carbons or conventional multiple tray designs used in series.

Current criteria prohibit the reuse of nonradioactively contaminated carbons, (67)(68) however, research is being conducted on regeneration and potential reuse of such carbons.(28)(58)

### VIII. Mechanical Arrangements

The US practice evolved primarily around shallow beds of impregnated activated carbon (5.0 cm bed depth), although numerous new installations use 10.0 to 20.0 cm bed depths, while in Europe many systems use 25.0 to 40 cm bed depths, although the variation of sophistication of iodine control systems in Europe is wider than in the US.(69)(70)(71)(72)(73)(82)(83)(84)

Engineered safeguard systems meeting NRC Regulatory Guide 1.52 criteria consist of prefilter/demister, HEPA filter, carbon bed, HEPA filter combinations, while nonsafeguard systems meeting NRC Regulatory Guide 1.14 consist of prefilter/demister, HEPA filter, carbon bed combinations.

ANSI N509 specifies internal space requirements for the systems, but only loose requirements exist for external serviceability of the iodine clean-up system and its modules. All systems should be evaluated for potential servicing in a radioactively contaminated stage. Access and servicing while protective clothing has to be worn and staging area for unloading contaminated adsorbers or adsorbent and speedily reloading the unit for availability is often inadequate. Filter/adsorber units are often hidden in space left over after other supposedly more important equipment is located.

Fire control systems installed have resulted in accidental deluges of adsorber systems upon false signal, making the adsorbent inefficient and causing serious corrosion, particularly in free iodine containing units. Aside from aging, this is the most common failure of iodine control units in the US. While the problem is known for at least four years, the frequency of accidental flooding has not decreased and better fire control methods have not been developed.

Even in proper application of cooling water on adsorbers loaded with radioactive iodine, the liquid rad waste units are often not designed to handle the large quantity of water contaminated with radioactive iodine. Transfer of such water to tanks which are contaminated with organic containing water will result in the generation of organic iodides into the atmosphere.

### IX. Inspection and Testing

While the requirement for test conditions finally reached the state of the art with the latest edition of ANSI N510, its implementation is still far from existence. Even the new test criteria for iodine removal efficiency based on ASTM D3803 will have to be subject to revision after some use when operating data is built up. However, most of the current Technical Specifications of power reactors specify test conditions which are rarely realistic of the potential adsorbent use conditions. Tests performed at high temperatures (55 - 180°C) even at high humidity will result in higher indicated  $\text{CH}_3^{131}\text{I}$

removal efficiencies, than the low temperature (25°C - 30°C) high humidity tests. Particularly the extensive preequilibration at 130°C, before loading methyl iodide onto the adsorbent, results in a very efficient regeneration of the adsorbent prior to the actual test of its efficiency.

The US practice is to establish bypass leak rates in place and remove a sample of the adsorbent for laboratory test of its removal efficiency for various iodine species.(25)(68)(74) The European practice in turn involves in place tests using methyl iodide tagged with  $^{131}\text{I}$ .(69)(70)(71)(72) Both practices can be useful if proper precautions are taken to assure that sampling is representative, and if external samplers are used, the exposure of the samples is identical to that of the main adsorbers.

While the sophistication of the technique of iodine adsorbent efficiency evaluation is increasing, often visually observed defects, also very important, are overlooked. Such observations as carbon falling out of adsorbers, or loosely tightened modules, corroded mild steel or occasionally corroded stainless steel components, which may result in gross failure of systems are not properly utilized for immediate corrective action.

#### X. Three Mile Island

Several important lessons were learned from the TMI-II accident relating to iodine control. The first one is that the iodine release and transport theories are incorrect. Most of the iodine stayed in the reactor phase or plated out in the containment. The total iodine which reached the operating filter adsorber trains can be estimated on the most conservative basis to be 150 Curies, of which approximately 15 - 32 Curies were released to the environment. This value when compared with approximately  $13 \times 10^6$  Curies of  $^{133}\text{Xe}$  released is a good indication of the lack of predicted partitioning of iodine species into the air stream. One indication of the iodine species distribution showed methyl iodide to be predominant, followed by elemental iodine and products identified as  $\text{HOI}$ .(78)(79)(80)(81)

The systems available for iodine release control were two trains in the Unit-II Auxilliary Bldg. identified as Trains A and B, and two trains in the Fuel Handling Bldg. identified as Trains A and B. The Auxilliary Bldg. trains were not classified as engineered safeguards and captured approximately 12 and 14.6 Curies of iodine and released approximately 1.2 to 1.8 Ci. The Fuel Handling Bldg. filters were downgraded safeguards and captured approximately 36 to 48 Ci. iodine respectively, and released approximately 5 and 15 Ci.

The performance of the Auxilliary Bldg. adsorbers was somewhat similar; 69.5% and 56.0% efficiency for methyl iodide. The pH values of the water extract showed 4.3 - 5.9 for Train A and 3.4 - 4.6 for Train B. The adsorbent in both beds was extensively poisoned and was impregnated with  $\text{KI}_3$ .

The performance of the Fuel Handling Bldg. trains showed up another problem with iodine clean-up units. While Train A had a 75.6% efficiency for  $\text{CH}_3^{131}\text{I}$ , Train B had only 49.1%. This anomaly was caused by a faulty damper system, which resulted in unbalanced flow between the two trains, permitting larger air flow through the B Train. That this condition existed even before the accident is shown by the water extract pH also. Train A had 4.1 - 4.7 pH while Train B had 3.4 - 3.9. The net result was that approximately 66% of the total release of the four systems has taken place through Train B of the Fuel

## 16th DOE NUCLEAR AIR CLEANING CONFERENCE

Handling Bldg.

The adsorbers in these trains were non-standard size, i.e. 40 inches long, versus the standard industry length of 26 - 30 inches, which created change-out problems, particularly when it was found out that nobody stocks spares of this size. Fortunately, approximately 150 adsorbers were ordered and delivered on site shortly before the accident. These adsorbers were filled with KI-Amine coimpregnated carbons and showed high efficiency for the three predominant methyl iodide species.

Change-out logistics was a problem, and at one time, a number of the initial adsorbers were removed without immediate replacement on a one for one basis, which resulted in additional iodine release through the gap in the adsorber banks.

Unfortunately, detail analysis of the reinstalled and the add-on filter systems, installed for a second 5.0 cm bed adsorbent protection, was involved in logistics problems by inadequate control on where and how samples were taken. The only sound conclusion that can be drawn that no significant amounts of iodine were released after the initial adsorbers were replaced and the supplementary banks installed.

The problems of iodine control at TMI-II were not the magnitude to cause serious consequences, because the iodine release and transport from the core did not follow TID 14844 predictions, if the iodine behaved in the highly conservative manner of regulatory expectations, the iodine releases would have been much more significant.

The problems which existed at TMI-II in relation to the behavior of the adsorbent and the adsorber units were known to the industry. Prior documents, papers at Air Cleaning Conferences pointed out every one of the inadequate protection areas, without effective change being accomplished at the use site.

Even today, there are many iodine control systems that are downgraded because of NRC exceptions granted, there are KI<sub>3</sub> impregnated acidic carbons installed, there are tests being performed under conditions unrealistic for accident sequence, there are dampers installed which are inadequate for flow control, there are no spares or inadequate numbers on site, and no tests performed on so-called non-safeguard systems (75)(76)(77)

### XI. Summary and Conclusion

The evolution of the iodine control technology in the US has been in response to events which are not necessarily realistic in conservatism or in predicted performance of the systems. The form of iodine released, its transport and partitioning into airborne, waterborne and deposited forms by source term documents does not follow the values found in real life. The development and application of adsorbents does not consider all of the factors involved in case of operational or accidental iodine control.

While significant improvements were made in hardware and adsorbent efficiencies, the application of an integrated technology and realistic regulatory criteria are lacking. The segmentation of responsibility in research, design, review, development, construction, testing and operation results in periodic misapplication and great gaps between identification of problem areas and their correction.

## 16th DOE NUCLEAR AIR CLEANING CONFERENCE

The formation of a task group involving all relevant parties from iodine release to disposal should be formed with participation of the researchers, designers, builders, regulators, and users to assure that integrated technology is applied on a sound engineering basis.

### References

1. G. W. Keilholtz and C. J. Barron, "Behavior of Iodine in Reactor Containment Systems", ORNL-NSIC-4, February 1965.
2. G. W. Parker and C. J. Barton, "Fission Product Release, 18. The Technology of Nuclear Reactor Safety", MIT 1973.
3. "Halogen Collector Test Program", Arthur D. Little, Inc., Report HW-65587, ALI-54, March 1960.
4. Leslie Silverman, Richard Dennis, Edward Kristal, and Felix Stein, "Iodine Collection Studies", AEC Report TID-7593, July 1959.
5. R. Dennis, L. Silverman, and F. Stein, "Iodine Collection Studies", AEC Report TID-7677, Vol. 2, October 1961.
6. J. A. Riley, "The Containment of Fission Products in a Power Reactor", AEC Report TID-7677, Vol. 2, October 1961.
7. F. G. May, "Comparison of Charcoals in Removing Iodine from Air-Streams at High Temperature", Report AERE-R 4145, 1962.
8. Robert E. Adams and William E. Browning, Jr., "Removal of Iodine from Gas Streams", AEC Report TID-7627, Vol. 1, October 1961.
9. J. Pradel, G. Chevalier, and F. Billard, "Etude de l'Arret de l'Iode par les Charbons Actifs", Service de Controle des Radiations et de Genie Radioactif Report CEA No. 2237, 1963.
10. C. H. Prigge, "Application of Activated Carbon in Reactor Containment", DP-778, September 1962.
11. W. S. Durant, R. C. Milham, D. R. Mulhbaier, and A. H. Peters, "Activity Confinement System of the Savannah River Plant Reactors", USAEC Report DP-1071, August 1966.
12. R. E. Adams, W. E. Browning, Jr., W. B. Cottrell, and G. W. Parker, "The Release and Adsorption of Methyl Iodide in the HFIR Maximum Credible Accident", USAEC Report ORNL-TM-1291, October 1965.
13. A. C. Chamberlain, A. E. J. Eggleton, W. J. Megaw, and J. B. Morris, "Physical Chemistry of Iodine and Removal of Iodine from Gas Streams", Reactor Science and Technology (J. Nuclear Energy, Parts A and B), 17 519, 1963.
14. W. J. Megaw and F. G. May, "The Behavior of Iodine Released in Reactor Containers", Reactor Science and Technology (J. Nucl. Energy, Parts A and B)

## 16th DOE NUCLEAR AIR CLEANING CONFERENCE

Trapping of Fission Product Iodine", AEC Report CONF-700816, August/September 1970.

33. D. T. Pence, F. A. Duce, and W. J. Maeck, "A Study of the Adsorption Properties of Metal Zeolites for Airborne Iodine Species", AEC Report CONF-700816, August/September 1970.
34. L. R. Jones, "Effect of Gamma Radiation on Adsorption of Iodine and Methyl Iodide on Activated Carbon", AEC Report CONF-700816, August/September 1970.
35. R. D. Ackley and R. E. Adams, "Effect of Containment Spray Solution on Trapping of Radioactive Methyl Iodide from Flowing Steam-Air by Iodized Charcoal", U.S. Atomic Energy Commission Report ORNL-TM-2805.
36. R. E. Adams, R. D. Ackley, and W. E. Browning, Jr., "Removal of Radioactive Methyl Iodide from Steam Air Systems", USAEC Report ORNL-4040, January 1967.
37. J. L. Kovach and J. R. Hunt, "Iodine Fission Product Mass Transfer in Adsorbent Media", AEC Report CONF-740807, Volume 1, August 1974.
38. V. R. Dietz, C. H. Blachly, and L. A. Jones, "Dependence of Gas Penetration of Charcoal Beds on Residence Time and Linear Velocity", ERDA Report CONF-760822, August 1976.
39. W. Jost, "Diffusion in Solids, Liquids, Gases", Academic Press, 1960.
40. "Connecticut Yankee Charcoal Filter Tests", CYAP-101, December 1966.
41. J. B. Morris and C. H. Romary, "Tests on Adsorbers for Iodine at Low Concentrations", Atomic Energy Research Establishment, Harwell Report AERO-R 4219, February 1963.
42. C. E. Graves, J. R. Hunt, J. W. Jacox, J. L. Kovach, "Operational Maintenance Problems with Iodine Adsorbers in Nuclear Power Plant Service", DOE Report CONF-780819, Volume 1, August 1978.
43. J. L. Kovach, L. Rankovic, "Evaluation and Control of Poisoning of Impregnated Carbons Used for Organic Iodide Removal", DOE Report CONF-780819, Volume 1, August 1978.
44. D. A. Collins, L. R. Taylor, and R. Taylor, "The Development of Impregnated Charcoals for Trapping Methyl Iodide at High Humidity", British TRC Report 1300(W), 1967.
45. V. R. Dietz and C. H. Blachly and A. G. Evans, "New Charcoal Impregnants for Trapping Methyl Iodide - (I) Salts of the Iodine Oxyacids with Iodide or Iodine and Hexamethylenetetraamine; (II) Applications to a Variety of Base Charcoals", ERDA Report CONF-760822, August 1976.
46. Nuclear Consulting Services, Inc. US Patent Application 112,934, 1980.
47. R. A. Lorenz, S. R. Manning, and W. J. Martin, "The Behavior of Highly Radioactive Iodine on Charcoal in Moist Air", ERDA Report CONF-760822, August 1976.
48. Personal Communication from V. R. Dietz to J. L. Kovach, 1978.

16th DOE NUCLEAR AIR CLEANING CONFERENCE

- 16, 427, 1962.
15. D. A. Collins, L. R. Taylor, and R. Taylor, "Development of Impregnated Charcoals for Trapping Methyl Iodide at High Humidity", AEC Report CONF-660904, Vol. 1, September 1966.
  16. A. G. Evans, "Effect of Alkali Metal Content of Carbon on Retention of Iodine at High Temperatures", AEC Report, CONF-740807, Vol. 1, August 1974.
  17. A. G. Evans, "Effect of Service on Retention of Iodine by Activated Carbon", AEC Report CONF-700816, August/September 1970.
  18. J. Louis Kovach, "Adsorbents; Review and Projection", AEC Report CONF-680821, August 1968.
  19. R. D. Ackley and R. E. Adams, "Aging and Weathering of Impregnated Charcoals Used for Trapping Radioiodine (An Interim Report)", AEC Report CONF-680821, August 1968.
  20. J. L. Kovach and R. G. Newton, "Deep Bed Activated Carbon for Liquid, Solid, Aerosol and Gaseous Filters", AEC Report CONF-700816, August/September 1970.
  21. H. L. Barnebey, "High Efficiency Gasketless Adsorber", AEC Report CONF-720823, August 1972.
  22. H. C. Parish, L. E. Schuermann, D. P. Siegwarth, "Development and Performance Evaluation of an Improved Standby Gas Treatment System for Enrico-Fermi - Unit 2", AEC Report CONF-740807, Volume 1, August 1974.
  23. J. J. DiNunno, F. D. Anderson, R. E. Baker, and R. L. Waterfield, "Calculation of Distance Factors for Power and Test Reactor Sites", USAEC Report TID-14844, March 1962.
  24. USNRC Regulatory Guide 1.3, 1.4, and 1.25.
  25. USNRC Regulatory Guide 1.52, Rev. 2.
  26. USNRC Regulatory Guide 1.140, Rev. 1, 1979.
  27. J. L. Kovach and J. E. Green, "Evaluation of the Ignition Temperature of Activated Charcoals in Dry Air", Nuclear Safety, V8 No. 1, p.41, 1966.
  28. A. G. Evans, "Effect of Service Aging on Iodine Retention of Activated Charcoal", ERDA Report CONF-760822, August 1976.
  29. A. G. Evans, "Effect of Intense Gamma Radiation of Radioiodine Retention by Activated Carbon", AEC Report CONF-720823, August 1972.
  30. L. R. Jones, "Effect of Gamma Radiation on Adsorption of Iodine and Methyl Iodide on Activated Carbon", AEC Report CONF-680821, August 1968.
  31. W. J. Maeck, J. H. Keller, H. R. Beard, and F. O. Cartan, "Inorganic Adsorbers for Samplers to Differentiate Inorganic and Organic Iodine Species", AEC Report CONF-680821, August 1968.
  32. J. G. Wilhelm and H. Schuettelkopf, "Inorganic Adsorber Materials for

## 16th DOE NUCLEAR AIR CLEANING CONFERENCE

49. G. W. Parker, G. E. Cheek, and A. Ferreli, "Retention of Methyl Iodide by Impregnated Carbons Under Ambient Conditions", AEC Report CONF-660904, Vol. 1, September 1966.
50. R. A. Lorenz, W. J. Martin, H. Nagao, "The Behavior of Highly Radioactive Iodine on Charcoal", AEC Report CONF-740807, Volume 1, August 1974.
51. V. R. Dietz and J. B. Romana, "Iodine Emission During a Programmed Heating of Impregnated Charcoals in Carrier Air", ERDA Report CONF-760822, August 1976.
52. R. J. Davis and R. D. Ackley, "Long-Term Effects on Radioiodine Trapping by Charcoal", AEC Report CONF-720823, August 1972.
53. D. T. Pence and B. A. Staples, "Solid Adsorbents for Collection and Storage of Iodine-129 from Reprocessing Plants", AEC Report CONF-740807, Volume 1, August 1974.
54. D. T. Pence, F. A. Duce, W. J. Maack, "Developments in the Removal of Airborne Iodine Species with Metal-Substituted Zeolites", AEC Report CONF-720823, August 1972.
55. R. P. Shields, "Ignition of Charcoal Adsorbers by Fission Product Decay Heat", AEC Report CONF-700816, August/September 1970.
56. E. A. Bernard and R. W. Zavadoski, "The Calculation of Charcoal Heating in Air Filtration Systems", AEC Report CONF-740807, Volume 1, August 1974.
57. K. Bratzler, "The Autoignition of Carbons as a Process Problem", Chem. Ing. Tech., p.569, 1956.
58. J. R. Hunt, L. Rankovic, R. Lubbers, and J. L. Kovach, "Iodine Removal Adsorbent Histories, Aging and Regeneration", ERDA Report CONF-760822, August 1976.
59. R. R. Bellamy and V. R. Deitz, "Confirmatory Research Program - Effects of Atmospheric Contaminants on Commercial Charcoals", DOE Report CONF-780819, Volume 1, August 1978.
60. L. R. Taylor and R. Taylor, "The Ageing of Impregnated Charcoals", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, December 1973, p. 121.
61. N. Stead, "Experience in Testing Iodine Sorption Plants Associated with CEGB Gas-Cooled Reactors", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 391, December 1973.
62. J. G. Wilhelm, H. G. Dillmann, and K. Gerlach, "The Testing of Iodine Filter Systems", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 211, December 1973.
63. G. Van del Lugt and L. C. Scholten, "Methods Used at KEMA for Measuring Iodine Adsorption on Charcoal and Experience with Charcoal Filters Installed at a Nuclear Power Plant," Seminar on Iodine Filter Testing, Vol. 1, p. 315, December 1973.



## 16th DOE NUCLEAR AIR CLEANING CONFERENCE

64. R. Hesbol, B. Normann, and L. Devell, "Iodine Filter Testing in Sweden", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 329, December 1973.
65. J. J. Hillary and L. R. Taylor, "Experience at Windscale of Full Scale Iodine Sorption Plant Testing with Methyl Iodide", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 361, December 1973.
66. J. R. D. Stoute and G. C. Groen, "Experiences with Charcoal Filter Systems Installed in Several Buildings at the R.C.N. Site", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 503, December 1973.
67. Standard Method of Radioiodine Testing of Nuclear Grade Gas Phase Adsorbents, ASTM 03803, 1979.
68. Nuclear Power Plant Air Cleaning Units and Components, ANSI N509, 1979.
69. J. G. Wilhelm, H. G. Dillmann, K. Gerlach, "Testing of Iodine Filter Systems Under Normal and Post-Accident Conditions", AEC Report CONF-720823, August 1972.
70. J. J. Hillary, "Iodine Sorption Plant Test Procedures in the United Kingdom", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 237, December 1973.
71. P. Sigli and L. Trehen, "Iodine Trap Testing in Nuclear Power Stations", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 259, December 1973.
72. M. Gence, "Iodine Trapping Plant Testing at the Nuclear Power Stations of Electricite de France", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 415, December 1973.
73. R. W. Zavadoski, H. Gilbert, A. B. Fuller, and C. A. Burchsted, "Engineered Safety Features Air Cleaning Systems for Commercial Light-water-cooled Nuclear Power Plants (A review of current design and construction practices)", AEC Report WASH-1234 (UC-80), June 1974.
74. Testing of Nuclear Air Cleaning Systems. ANSI N510, 1980.
75. Nuclear Consulting Services, Inc., "Analysis of the Adsorbers and Adsorbents from Three Mile Island Unit 2", NUCON 6MT611/09, June 11, 1979.
76. Nuclear Consulting Services, Inc., "Iodine-131 Removal Efficiency Determination of Adsorbent Samples", NUCON 6MT611/12, 1979.
77. "Three Mile Island, A Report to the Commissioners and the Public", Vol. II, Part 2, M. Rogovin, Director (1980).
78. R. R. Bellamy and F. P. Cardile, Editors, "Calculation of Releases of Radioactive Materials in Gaseous and Liquid Effluents from Boiling Water Reactors (BWR GALE Code)", NUREG-0016 Rev. 1, 1979.

## 16th DOE NUCLEAR AIR CLEANING CONFERENCE

79. Barrett, L. H., NRC Memorandum "Preliminary Estimates of Radioactive Releases from Three Mile Island", 1979.
80. H. Lawroski, "Technical Staff Analysis Report on Transport of Radioactivity from the TMI-2 Core to the Environs to Presidents Commission on the Accident at Three Mile Island", 1979.
81. W. R. Stratton, A. P. Malinauskas, R. O. Campbell, letter to Chairman Ahearne of the USNRC, 1980.
82. H. H. Stiehl, M. Neumann, and D. Sinhuder, "Air Filtration Plants of Wall-Type for Separation of Fission Iodine in Nuclear Reactors", ERDA Report CONF-760822, August 1976.
83. W. A. Emel, D. C. Hetzer, C. A. Pelletier, E. D. Barefoot, and J. E. Cline, "An Airborne Radioiodine Species Sampler and its Application for Measuring Removal Efficiencies of Large Charcoal Adsorbers for Ventilation Exhaust Air", ERDA Report CONF-760822, August 1976.
84. H. Strauss, G. Staschik, and K. Winter, "Iodine Sorption Plants for Nuclear Power Stations", Seminar on Iodine Filter Testing, Commission of European Communities, Vol. 1, p. 163, December 1973.

## DISCUSSION

EVANS: I have a question on TMI. Were the internal spray suppression units that were supposed to reduce the airborne activity in the dome activated or used such that the water that eventually found its way into the sumps was fairly highly alkaline?

KOVACH: The water was alkaline. This matter will be discussed in detail during the TMI section of the conference.

EVANS: The reason I asked the question is because a few years ago we did some experimental work at Savannah River, where we intentionally irradiated iodide salts in aqueous solution and found that under neutral conditions, as much as 17 to 34 percent of the iodide form of the iodine was converted to  $I_2$  because of the high G value for the iodide ion in solution. Thus, it could be revolatilized if there is not a basic solution from which it is being generated.

KOVACH: I certainly agree that there are conditions for which you can postulate accident modes where there would be slightly different conditions than what occurred at TMI. But, I am not looking only at TMI. You can go to almost any accident that occurred with any water-cooled reactor system and see that the iodine releases were orders of magnitude lower than what we are required to design for.

EVANS: I do not doubt that a very large portion of what starts out as elemental iodine is very readily converted to a whole spectrum of inorganic iodine salts. But, in the very intense radiation environment, it is possible to convert a large fraction of these back into elemental iodine, which can be volatilized again.

KOVACH: I agree, and I think that for an iodine cleanup technology, we should also look at iodine control in the pool of water in the reactor containment, in case of an accident. That is very much a part of iodine control and, in some ways, it would be much easier to control and prevent releases into the atmosphere than to worry about hundreds of thousands of cfm that we have to treat.

WILLIAMS: You mentioned that one of the species identified as being released from TMI was hypoiodous acid, HOI. How firm was this confirmation?

KOVACH: I said that some people had identified HOI. I think that some of the HOI that we are seeing is a result of the sampler and not necessarily a result of the species being actually present in the airborne environment. I will let people who are more confident about hypoiodous acid discuss it in more detail. It was stated that in some cases up to a quarter of the iodine was identified as HOI, but I am not convinced.

HILLIARD: I think you did a good review, but I think you also missed a large segment of the literature dealing with wet chemistry reactions of iodine in primary water, containment spray, etc. I have a question. At TMI-2, where the iodine in the primary system was obviously at equilibrium, the only escape was by liquid primary water vented through the relief valve or let-down system. And then the iodine came to a new equilibrium in the containment and auxiliary buildings. Did you calculate a partition coefficient for the iodine in the gas and liquid phases?

KOVACH: Only very briefly. The feed data became available so late that it could not be incorporated into this paper. Part of this paper was already written when detailed information came out. However, I still think that if we analyze the data as now available, we will still see that iodides are formed, not only in that case but in many others. I am stressing that I am not looking only at TMI.

HILLIARD: My point is that you have mentioned several times that this was very unexpected. I think it is just about what you would expect with our present knowledge of partition coefficients. The fact was that primary water was released rather than primary gases. In other words, the fact that TMI and all the other accidents that you have examined did not involve releases of iodine according to the old TID 14844 assumption does not mean that larger releases could not happen, with a large pipe break and a gaseous release.

KOVACH: I think that the possibility exists to have accident modes that would release significantly more iodine than TMI did, but nothing near the currently stated criteria to which we are designing.

HILLIARD: This is your statement, but I think it needs to be substantiated.

PENBERTHY: You have talked about the capture of iodine. After you have captured it, then what is the ultimate disposition?

16th DOE NUCLEAR AIR CLEANING CONFERENCE

KOVACH: Xenon.

PENBERTHY: Just decay?

KOVACH: Yes.

PENBERTHY: Is there any need for a fixation process that would be considered permanent? How long do you have to store it in order to consider it as disposed of?

KOVACH: I do not think storage for iodine-131 is a relevant technology to investigate.

FLUKE: You brought up the subject of HOI. Did you have the opportunity to test the charcoal filters for HOI absorption? If so, what were the results?

KOVACH: Yes. On the HOI efficiencies of the impregnated carbons it was quite high. The species was also analyzed by SAI. I think that a part of the results was shown in the Rogovin report.

DEUBER: What is the experience on desorption of elemental iodine from activated carbon at ambient temperature? Normally, we speak of desorption at higher temperatures, but what about ambient temperature?

KOVACH: There were indications on the used carbon at TMI that they were bleeding iodine. I think Dr. Dietz may have a little more data on how much of the bleedout was in elemental and how much was in a methyl form, and he may be covering it in his paper. I know that he looked at the bleedout. We will have a paper from NUCON later on, discussing what we found using methyl iodide and some elemental iodine on the bleedthrough. We were seeing bleedthrough on both.

WILHELM: I am a little afraid that we may go from one extreme, which was an accident of an air-cooled reactor at Windscale, to the other extreme, which was the experience at Three Mile Island. At Three Mile Island, the release of iodine was along a pathway which was by no means typical for most of the sequences of events of the design basis accident. In the first case, at Windscale, we had air cooling of the core and a release directly to the atmosphere; this means a dry, oxidizing environment. At Three Mile Island, chemists would compare the release pathway with two wash bottles in line to wash the iodine out of the atmosphere with water. The first was the pressurizer and the second the blowdown tank. With both, one will get complete mixing of iodine and water. If we now go from one extreme of the release conditions to the other in our assumptions for the release and behavior of fission products during an accident, we won't be on the right scale. And because I have seen letters from American scientists to NRC, that are already being distributed in Germany, pointing to extreme low release experienced under certain light water reactor conditions, it may increase the overreaction. I would just like to say that one should not go too far now to the other side. To give an example, in German regulations we assume 2.5% iodine of the core inventory in an airborne form in the containment for the design basis accident; this is to be compared with 25% in the US. Considering recent data, we may decrease the 2.5% by a factor of, maybe, 5-10, but I think that is then the end of the line.

## 16th DOE NUCLEAR AIR CLEANING CONFERENCE

KOVACH: I agree with your conclusion that we should not jump from one extreme to the other, but I think we should know the integration limits of our potential releases and not design for either one or the other, but be able to handle any of the conditions. And I would like to mention that I do not consider myself an expert on iodine transport. My criticism is not for the people performing the experiments, but more for the people misapplying the results of those experiments.